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(57) Abstract: Embodiments of the polymerization process of the present invention are directed to polymerizing free radically polymerizable monomers in the presence of a polymerization medium initially comprising at least one transition metal catalyst and an atom transfer radical polymerization initiator. The polymerization medium may additionally comprise a reducing agent. The reducing agent may be added initially or during the polymerization process in a continuous or intermittent manner. The polymerization process may further comprise reacting the reducing agent with at least one of the transition metal catalyst in an oxidized state and a compound comprising a radically transferable atom or group to form a compound that does not participate significantly in control of the polymerization process. Embodiments of the present invention comprise reacting a reducing agent with at least one of catalyst in an oxidized state and a compound comprising a radically transferable atom or group to initiate and/or maintain catalytic activity throughout the polymerization process.

